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A Study of Cobaltinitrites & their
Application to Analytical Chemistry

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A STUDY OF COBALTINITRITES AND THEIR
APPLICATION TO ANALYTICAL CHEMISTRY

BY

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B. S. University of Illinois, 1911

THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Oliver Kamm

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DEGREE OF

Master of Science in Chemistry

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Recommendation concurred in:

Committee

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A STUDY OF COBALTINITRITES AND THEIR APPLICATION
TO ANALYTICAL CHEMISTRY

The results of a preliminary study of cobaltinitrites have been presented in a previous thesis.¹ In a second treatment of the subject it is intended, by way of introduction, to present very briefly the results of the above mentioned work, so as to render unnecessary a reading of the details of the first thesis. The somewhat cumbersome historical review of the literature of the subject given in the latter will be partly dispensed with in the present case. References to all important work on cobaltinitrites will be given, altho mainly in connection with the experimental work. It is hoped in presenting this more congenial review of the literature, to show the relation of the latter to each part of the subject in question instead of presenting it as an isolated chapter. For a detailed historical review of the early literature, the reader is referred to the first paper.

Attention is directed to a preliminary publication² on this subject. The article is embodied in the present thesis,

1. O. Kamm. B.S. Thesis, Univ. of Ill. 1911.
2. Burgess and Kamm. J. Chem. Soc. 34, 652 (1912).

as is also a second paper dealing with the use of cobaltinitrites in quantitative analysis, the publication of which has been withheld until the reinvestigation of some of the early work on the subject.¹

The precipitate formed by the addition of the soluble sodium cobaltinitrite, $\text{Na}_3\text{Co}(\text{NO}_2)_6$, to a solution containing potassium has long been recognized as a delicate qualitative test for the latter. Dr. De Koninck² was probably the first to make this application. Later it was found convenient to precipitate potassium in this manner, completing the quantitative determination by some other method, after the separation of the cobalt, weighing the potassium as platonic chloride or as sulphate.

The use of the same reaction as a qualitative test will be found described in most text-books on Qualitative Analysis. Bray³ has shown that the test is delicate enough to detect sixty parts of potassium per million, provided a large excess of reagent is used. Recently, Bowser⁴ has increased its sensitiveness by precipitating in the presence of ethyl alcohol. A similar reaction, depending upon the formation of the tripotassium salt, $\text{K}_3\text{Co}(\text{NO}_2)_6$, is commonly used in the analytical laboratory for the detection of cobalt in the presence of nickel. As little as two parts of cobalt per million may be detected in this way. The method was originally proposed by Fischer⁵ in 1848.

1. See pp. 38 of this thesis.

2. Macallum, J. Physiol., 32-95 (London).

3. J. Am. Chem. Soc., 31, 613-621-633 (1909).

4. Ibid, 33, 1566, 1752 (1911).

5. Pogg, Ann. 74, 124 (1848).

In 1900, Adie and Wood¹ demonstrated the possibility of employing the cobaltinitrite method for potassium as a rapid and accurate volumetric process, and since that time much work has been done to bring it to perfection. The solution of this problem is of prime importance to agricultural chemists and consequently the activity in this field has been confined mainly to them. The work of Drushel¹, Bowser³, and Shedd⁴ is typical. All of them have attempted to apply the di-potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, to the determination of potassium, the method of each being based upon some modification of the original method of Adie and Wood. The last mentioned investigators proposed to determine the amount of potassium present by means of direct oxidation of the nitrite itself, using potassium permanganate solution. After the precipitation of the potassium as cobaltinitrite, the latter was decomposed in alkaline solution, the cobaltic hydroxide filtered out and the nitrite oxidized by the addition of N/10 $KMnO_4$. Assuming the substance to be $K_2NaCo(NO_2)_3$, each cubic centimeter of exactly N/10 $KMnO_4$ is equal to .0007856 gm. of K_2O . Drushel has suggested that the precipitate be decomposed directly in hot $KMnO_4$ solution, thus necessitating no separation of cobalt. Since however, cobalt will be reduced from the cobaltic to the cobaltous

1. *I. Chem. Soc.*, 77, 1076 (1900).

2. *Am. J. Sci.*, 24, 433 (1907); 26, 329; 26, 555 (1908); *Chem. News* 97, 124 (1908).

3. *J. Ind. and Eng. Chem.*, 1, 791 (1909); *Chem. News*, 101, 100, (1910); *J. Am. Chem. Soc.*, 32, 78 (1910).

4. *J. Ind. and Eng. Chem.*, 1, 302 (1909); 2, 379 (1910).

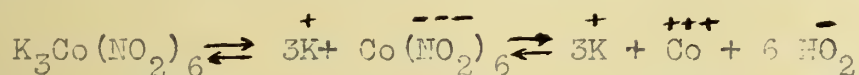
state during the titration, our factor for the calculation of K_2O becomes .0008573, or twelve elevenths of what it was in the case when cobalt did not exert its oxidizing power. Very recently MacDougall¹ has suggested a method of titration in acid solution. According to him cobaltic cobalt will not oxidize nitrous acid in acid solution and consequently total nitrite will be titrated. His conclusions are, however, based upon insufficient data, only four titrations having been made. In repeating his work, using the silver potassium cobaltinitrites described below, it was found that identical results were obtained irrespective of whether the titration was conducted in acid or neutral solution.

Notwithstanding a good deal of careful work, results obtained with the use of the cobaltinitrite method have proven far from satisfactory, in fact, results show that an error of five percent may be looked for even in duplicate analyses. The experiments of the Official Agricultural Chemists² show almost identical variations. For this reason a rather extensive theoretical study of the method was made, with the hope of overcoming the difficulties now encountered in its application to analytical work. The method of attack has been from the physico-chemical standpoint, the object being to study the behavior of cobaltinitrites when in solution. The results of this investigation have been presented in the thesis already referred to³, and only a brief summary will be given here.

1. J. Am. Chem. Soc. 34, 1634 (1912).
2. J. Ind. and Eng. Chem. 2, 551.
3. O. Kamm, B.S. Thesis, 1911.

(1). It was shown that an accurate determination of potassium, using the sodium potassium cobaltinitrites, is impossible. One explanation for this lies in the fact that under the conditions of the experiment, we obtain a mixed precipitate composed of various sodium potassium salts, instead of the desired one, $K_2NaCo(NO_2)_6$. It was also shown that from more dilute solutions the tripotassium salt, $K_3Co(NO_2)_6$, was obtained. The results above mentioned are verified by the investigations made by Cunningham and Perkins¹, who also conclude that the cobaltinitrite method, in its present form, is not applicable to an exact determination of potassium.

(2). The solubilities of several cobaltinitrites were accurately determined, not only in water, but also in solutions of sodium and potassium salts. It was clearly demonstrated that solubility is accompanied by decomposition; thus,



and that very little of the unstable complex ion, $\overset{---}{Co(NO_2)_6}$, is present at any one time. (See also pp. 13 of this paper). The fact that we are measuring decomposition, and not absolute solubility, explains the fact that the observed solubility increases directly with time, and directly with the amount of surface exposed to the solvent. These points were not understood by previous investigators (Adie and Wood, Drushel, Bowser, and Rosenblatt²), all

1. J. Chem. Soc. 95, (pt. 2), 1562-69.

2. Ber. 19, 2531.

of whom, as would be expected, present very conflicting data in regard to solubility measurements, the values for the di-potassium salts varying from one part in 1120 to one part in 30,000.

(3). The statement in regard to the instability of the complex ion, $\text{Co}(\text{NO}_2)_6^{3-}$, was completely verified by means of conductivity determinations.

(4). The discovery of the insoluble silver-potassium cobaltinitrites was announced. A number of determinations were made using the latter, but certain conclusions were drawn in regard to their use in quantitative work, with insufficient data for doing so.

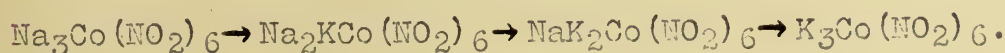
The present work has also shown that inaccurate conclusions had been drawn in regard to the composition of these silver potassium cobaltinitrites. During the continuation of the investigation, and its application to practical problems, it was found that conflicting results were obtained when applying the method under varying conditions. The source of these errors has been definitely located; i.e. when the silver potassium cobaltinitrites were washed with a dilute solution of potassium nitrate (the purpose being to decrease the solubility of the precipitate as well as to prevent it from passing into the colloidal condition), part of the silver was replaced by potassium. Moreover, since in this replacement a definite amount of silver was washed out, absolute checks were obtained in analyses carried out under the same conditions. The details of the present procedure will

be presented below.

THE USE OF SILVER POTASSIUM COBALTINITRITES AS
A DELICATE QUALITATIVE TEST FOR POTASSIUM

The reagent used in these qualitative tests is a solution of the sodium salt, $\text{Na}_3\text{Co}(\text{NO}_2)_6$, which may be prepared as described by Adie and Wood.¹ We have found it preferable, however, to use a solution of the pure substance, thus eliminating the large excess of sodium and cobaltous salts as well as acetic acid which, as will be shown later, interfere with the sensitivity of the reagent. The pure sodium salt may be prepared by precipitation with ethyl alcohol as described by Cunningham and Perkin². In the following experiments we have used a freshly prepared 25% solution of pure sodium cobaltinitrite.

When a drop of this reagent is added to a solution containing 1% of potassium, a yellow precipitate is formed immediately, which consists of tripotassium cobaltinitrite, $\text{K}_3\text{Co}(\text{NO}_2)_6$, or of the dipotassium salt, $\text{K}_2\text{NaCo}(\text{NO}_2)_6$, according to the amount of reagent used.³ In the presence of silver ion, however, the corresponding silver salts are formed. The entire series is represented here:



1. J. Chem. Soc. 77, 1076 (1900).

2. J. Chem. Soc. 95, 1562 (1909).

3. Ibid. (See also Gilbert, "Inaugural Dissertation," Tübingen, 1898.)



It would appear that as we replace sodium in the trisodium salt with potassium, we obtain less soluble substances. In the same manner if we replace sodium in the sodium-potassium derivatives, with silver, we obtain even less soluble salts--the silver-potassium cobaltinitrites. The delicacy of the latter reaction is shown by the following experiment: A drop of reagent added to a very dilute solution of potassium (less than 100 parts per million) produces no perceptible precipitate. If the test is repeated in the presence of 0.01 N silver nitrate, a copious yellow precipitate is formed immediately. In the absence of potassium nitrate, but using the same concentration of silver as before, it is found that the trisilver and the silver-sodium salts are not precipitated. Because of this fact it is possible to use these silver-potassium cobaltinitrites as a delicate qualitative reaction for potassium. In applying the test, it is essential that the solution be neutral or only slightly acidified with acetic acid. Halogens may be removed by the addition of silver nitrate, a large enough excess being added so as to obtain approximately a 0.01 N solution. Interference due to the presence of other substances is discussed below.

In the usual scheme of analysis the test may be applied after the removal of the heavy metals. The filtrate from the latter is acidified with an excess of nitric acid, evaporated to

dryness and the ammonium salts volatilized. The residue is extracted with water and the solution tested for potassium in the manner already described.

The silver potassium cobaltinitrite precipitate is very insoluble, in fact it serves to detect even less than one part of potassium per million. It comes down in a very finely divided condition, and examination under the microscope shows it to be amorphous. It exhibits a marked tendency to pass into the colloidal condition when washed with pure water but is coagulated by solutions of electrolytes. Alcohol serves the same purpose. The color of the precipitate varies from yellow to orange according to the conditions of the precipitation. Its composition also appears to be dependent upon these conditions; the larger the excess of silver present in the original solution, the more will be found in the precipitate. There is also a slight tendency for sodium to be carried down; the nature and extent of this contamination has been investigated and it has been shown that it will not interfere with a quantitative method. (See pp. 25 and 34.)

The delicacy of this qualitative test for potassium is shown by the following table. The fourth column represents approximately the time required for the decomposition of the precipitate, a phenomenon which accounts for the varying results obtained when determining the solubility of any cobaltinitrite. As would be expected, the precipitate is more stable in the presence of an increased volume of reagent.

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TABLE I

Parts potass- ium per million	Vol. $\text{Na}_2\text{Co}(\text{NO}_2)_6$ used	Precipitate appeared after	Precipitate lasted
3.0	1 drop	almost immediate	60 min.
2.0	1 drop	almost immediate	30 min.
1.0	1 drop	15 sec.	5 min.
0.5	0.5 cc.	2 min.	30 min.
0.2	1.0 cc.	turbidity after a min.	30

All of the above tests were made at a temperature of 15° , and the same concentration of silver nitrate (0.01 N) was used in every case.

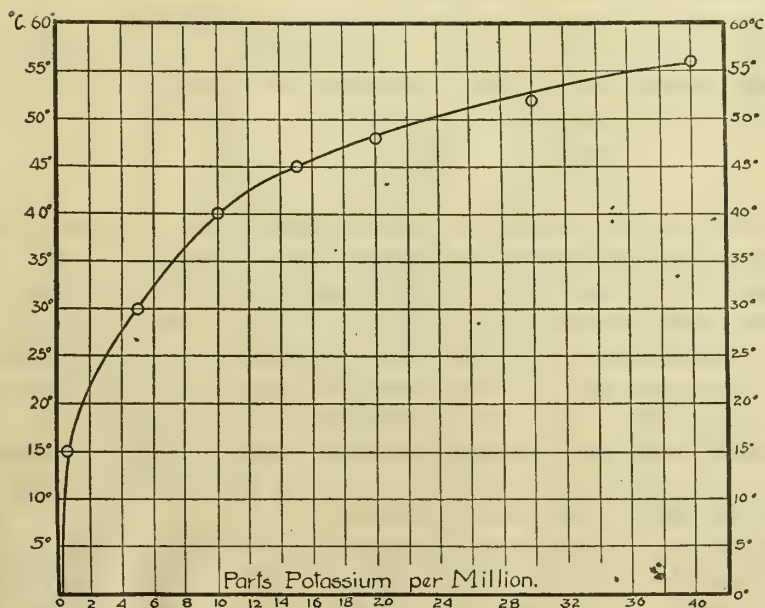
It is thus seen that the silver potassium cobalti-nitrite precipitate serves as an extremely delicate qualitative reaction for potassium. Its advantages over the old method are: (1) It is more sensitive.¹ (2) The test may be made with the use of a single drop of reagent added to 100 cc. of the solution.

When a mere trace of potassium is to be detected, the temperature of the solution must be considered, because of the rapid decomposition of the complex ion, $\text{Co}(\text{NO}_2)_6^{---}$. The latter is very unstable in dilute solutions and its rate of decomposition increases rapidly with increasing temperature. For example, at 15° we may detect one-half part of potassium per million. At a temperature of 30° , however, the limit of sensitiveness is five parts per million, while above 40° no precipitate is obtained

1. Although Bowser's modification is delicate enough to detect two parts of potassium per million, it possesses a distinct disadvantage in that no definite precipitate, but only a temporary turbidity is formed in such dilute solutions.

with ten parts, a single drop of reagent being used in each case.

The results of a series of experiments of this kind have been plotted, using the temperature as ordinate and the concentration of potassium as abscissa. The curve obtained represents graphically the effect of increasing temperature upon the delicacy of the test. The points on the curve represent the temperatures at which a known amount of potassium will just fail to produce a precipitate, the concentration of silver nitrate being 0.01 N. With the use of this curve we may make an approximate analysis of a solution containing potassium, by observing the temperature at which a temporary precipitate is formed. In the presence of sodium, however, the test would not prove very delicate. Only a few drops of reagent are added in order to avoid



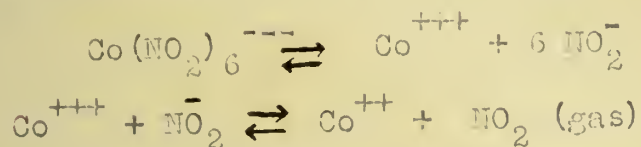
an excessive amount of sodium nitrite whose presence will interfere with the delicacy of the test. The explanation for this is given above.

The only substances interfering with this qualitative reaction for potassium are those that also interfere with the usual test in which the tripotassium salt is formed. Ammonia should be absent because it forms not only a triammonium salt¹ but also a less soluble salt containing silver. Rubidium, cesium, thallium, lead, and mercurous salts also interfere, as will be shown below. Barium forms sparingly soluble cobaltinitrites but the other alkaline earth metals do not. In concentrations below 0.1 N, barium will not interfere under the usual conditions.

In the dilute solutions used, sodium salts will not appreciably affect the delicacy of the test. When only a trace of potassium occurs in the presence of a tenth normal solution of sodium, the precipitate forms more slowly than usual, and it may be necessary to add a larger volume of reagent in order to secure complete precipitation. An increase in the amount of silver increases the delicacy of the test. Thus, any effect which is due to sodium may be counteracted by increasing the concentration of the silver. It is only when dealing with very dilute solutions of potassium, i.e., ten parts per million or less, that the effect of the sodium or of the silver ion need be considered.

1. Erdmann, J. prakt. Chem., 97, 404 (1866). Rosenheim and Koppel, Z. anorg. Chem., 17, 35 (1898).

In general, an excess of reagent increases the sensitiveness of the test provided that there has been no decomposition of the cobaltinitrite. This decomposition takes place in accordance with the following reactions, resulting in the increase in the concentration of nitrite ion.



The effect of the presence of a soluble nitrite, such as sodium nitrite, is to prevent the complete precipitation of the potassium. This is explained by the formation of the complex ion, $\text{Ag}(\text{NO}_2)_x$, with a consequent decrease in the concentration of silver ion. We have found that a certain definite concentration of the latter must be present in order to precipitate the silver potassium salt from a solution containing a given concentration of potassium. Since the addition of a nitrite removes silver ion from solution, we can, by adding a sufficiently large amount of the former, decrease the concentration of the latter to such an extent that the silver potassium salt will fail to be precipitated.

The following experiment will illustrate this point:

When a drop of reagent is added to a 0.01 N solution of silver nitrate containing ten parts of potassium per million, an immediate precipitate is formed. If, however, the experiment is repeated in the presence of a 0.1 N solution of sodium nitrite, no immediate precipitate is obtained under the same conditions, i.e., we have decreased the concentration of the silver ion to such a small

value that not enough is present to produce a precipitate. If a larger amount of potassium is present, or if an increased volume of reagent is added, a precipitate will be obtained. This is exactly what the law of mass action would lead us to expect.

Another interesting point may be brought out here. The silver cesium salt mentioned below is less soluble than the corresponding potassium salt. We would, therefore, expect it to be precipitated by a smaller concentration of silver ion than is needed to precipitate the potassium salt. This was actually found to be the case, i.e., when enough sodium nitrite was added to prevent the precipitation of the potassium salt, an equivalent amount of cesium, rubidium or thallium was still precipitated because of the smaller concentration of silver ion necessary.

It may be suggested that the silver potassium cobaltinitrites could be used as a delicate qualitative test for cobalt. They do not, however, offer any distinct advantage. The usual reaction, i.e., the formation of $K_3Co(NO_2)_6$, is very sensitive, due to the large concentration of potassium salts which decreases the solubility of the precipitate.

Other Insoluble Salts in this Series

The fact that potassium forms extremely insoluble cobaltinitrites led us to believe that other alkali metals would form similar silver salts. Considering the series Li, Na, K, Rb, and Cs, in which the elements are arranged in the order of increasing atomic weights, we find that the lithium and sodium

salts are very soluble while the potassium salts are rather insoluble. We would, therefore, expect the rubidium and cesium cobaltinitrites to be even less soluble, and Rosenblatt¹ has shown that this is the case. The following table shows the concentrations at which no precipitate was obtained when a drop of reagent was used. The results are, of course, only comparative, the test being more delicate when a larger volume of reagent is used.

TABLE II

	Concentration necessary for precipitation
K	100 to 150 parts per million
Rb	70 to 80 parts per million
Cs	70 to 80 parts per million
Tl	30 to 50 parts per million

Rubidium, cesium and thallium also form insoluble silver salts. Solutions of their salts so dilute that the reagent itself gives no precipitate readily form the characteristic insoluble yellow silver cobaltinitrites when in the presence of 0.01 N silver nitrate. They are all less soluble than the corresponding silver potassium salts, and like the latter may readily be precipitated from solutions containing less than one part per million (temp. 15° C.)

Ammonium salts also form an insoluble silver ammonium cobaltinitrite. The latter may be precipitated from solutions containing less than five parts of ammonia per million. This

1. Ber., 19, 2531 (1886).

would serve as a delicate qualitative test for ammonia in the absence of potassium.

Silver, lead and mercurous mercury all form cobaltinitrites. Of these, the silver salt, $\text{Ag}_3[\text{Co}(\text{NO}_2)_6]_2$,¹ and the lead salt, $\text{Pb}_3[\text{Co}(\text{NO}_2)_6]_2$,² have been described in the literature, but we have not been able to find any reference to their double salts with the alkali metals. The mercurous cobaltinitrite, probably $\text{Hg}_3\text{Co}(\text{NO}_2)_6$, has not, as far as we know, been described. It appears to be the least soluble of all the simple salts of the cobaltinitrite series.

Some of the double salts in the lead series are the lead ammonium, the lead potassium, the lead rubidium, the lead cesium, and the lead thallium salts. All of them are more soluble than the corresponding silver derivatives, but are less soluble than are the simple cobaltinitrites. It may be interesting to note here that we have also prepared a lead silver cobaltinitrite, which apparently stands intermediate between the lead and the silver series. It is less soluble than either the silver or the lead salt.

Rosenheim and Koppel³ have prepared the barium salt, $\text{Ba}_3[\text{Co}(\text{NO}_2)_6]_2$. We have found that barium also forms a barium silver salt. It is less soluble than the simple barium salt and may be precipitated from a tenth normal solution of barium pro-

1. Cunningham and Perkin, loc. cit.

2. Rosenheim and Koppel, loc. cit.

3. Loc. cit.

vised the concentration of silver is more than 0.01 M. It decomposes more readily than any of the other cobaltinitrites studied.

The barium and lead salts mentioned above are very sensitive to the conditions of the precipitation and their study may be of importance from this standpoint. They are crystalline in nature.

Cunningham and Perkin¹ have described certain cobaltinitrites containing organic radicals, such as the anilino-cobaltinitrite, $(C_6H_5NH_2)_3 - Co(NO_2)_6$. We have found the corresponding silver salts to be less soluble.

THE VOLUMETRIC DETERMINATION OF POTASSIUM

The slight solubility of the silver potassium cobaltinitrite precipitate made it an attractive one to study for the purpose of perfecting a procedure for the quantitative determination of potassium. Unfortunately, however, the composition of the precipitate is not constant, but varies slightly with the conditions under which it is precipitated. Results of analyses seem to show that no simple formula will be found to represent its composition; also, that no constant ratio exists between the quantities of silver and potassium in the compound. There is, however, a constant relation between the total silver plus potassium, expressed in gram atoms, and the total nitrite, expressed in gram equivalents, as is shown below. This fact makes

1. Loc. cit.

it possible to use this precipitate for the quantitative estimation of potassium, since both the silver and the nitrite may readily be determined.

Gilbert ¹ has shown that a somewhat similar constant relation between sodium plus potassium and nitrite, exists in the sodium potassium cobaltinitrites obtained in the precipitation of potassium by means of sodium cobaltinitrite. (DeMoninck's reagent).

Because of the fact that no rapid method is available for the determination of sodium in the presence of potassium, it is evident that any method which uses this precipitate can never give more than approximate results.

Relation between Metals and Nitrite

It has been stated that a constant relation exists between the total metals (silver plus potassium) and nitrite. Since the cobalt is in the cobaltic condition, part of the nitrite is oxidized by the cobalt during the titration with permanganate. Since, however, the ratio of cobalt to nitrite is also constant, there must exist a constant relation between the total metals and the nitrite determined by titration. This relation was obtained in the following manner.

Ten cubic centimeters of a standard potassium nitrate solution, containing 2.000 grams of potassium per liter, were measured out and diluted. Enough tenth normal silver nitrate was

1. Gilbert. Inaugural Dissertation. Tübingen, 1893.

added to make it approximately two-onehundredths normal in respect to silver, the final volume being 100 cubic centimeters. The potassium was precipitated with a concentrated solution of sodium cobaltinitrite, and the analysis completed as described in the outlined method given below. The results are recorded in Table 3.

Table III

No.	Amt. K	Cc. N/10 KMnO_4	Cc. NaCNS .02534 N.	Amt. NO_2	Amt. Ag	Ratio (Ag^+ K): NO_2
1	.0200 gm.	41.29 cc.	22.40 cc.	.09497 gm.	.06124 gm.	1:1.91
2	.0200	39.69	21.00	.09129	.05742	1:1.90
3	.0200	40.98	22.40	.09425	.06124	1:1.90
4	.0200	39.63	21.00	.09115	.05742	1:1.90
5	.0200	41.62	22.90	.09573	.06261	1:1.91

The above results show that the ratio given in the last column is constant, and may therefore be used as the basis for a quantitative method. This ratio (Metal: Nitrite = 1:1.90) was employed in all subsequent analyses, which were carried out according to the procedure given below. A glance at Table 4 will show that the concentration of potassium may be varied between wide limits without seriously influencing this ratio.

Method of Analysis

The reagent used is an approximately 25% solution of sodium cobaltinitrite, $\text{Na}_3\text{Co}(\text{NO}_2)_6$. It is prepared directly before using by dissolving the solid sodium salt [#] in water and

The reagent, sodium cobaltinitrite, may be obtained from various chemical houses if desired. It may be prepared as follows: 100 grams of cobalt acetate $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$

and 250 grams of sodium nitrite are dissolved in about 600 cc water. 100 cc. glacial acetic acid is then added, and, when thorough oxidation has taken place, the mixture is filtered to separate out as much of the insoluble potassium salt as possible. The trisodium salt is precipitated by the addition of several volumes of 95% ethyl alcohol, the voluminous precipitate being immediately filtered off (by suction) upon a large Büchner funnel, a double filter paper being used. After drying on a clay plate for a day, the reagent is ready to be bottled. Yield = about 120 grams, which is 75% of theory.

It has been customary in earlier work on this subject, to use the reagent without the precipitation and purification with alcohol. Whether or not this procedure will have an effect upon a quantitative method, must be shown in later work. All of the results recorded in this article were, however, obtained with the use of the pure reagent.

filtering through a thick asbestos mat in order to separate any potassium present.

Precipitation is effected by adding the reagent slowly from a pipette with constant stirring, to a dilute neutral solution containing potassium, an excess of silver nitrate being present. The concentration of the latter should not be greater than .02 normal, in order to prevent silver nitrite from being precipitated, the solubility of which is .027 mols per liter at 18° C. A relatively large excess of reagent is used [#]so as to insure complete precipitation.

[#] The fact that the filtrate shows the reagent color is no satisfactory criterion of complete precipitation, because of the partial decomposition of the reagent into the cobaltous condition, in which state no insoluble potassium silver salt is formed. Precipitation should take place at room temperature (about 20° C.), because of the ease of decomposition of all cobaltinitrites at a higher temperature.

The yellow silver potassium cobaltinitrite comes down in a finely divided condition, but may be filtered on a Gooch after standing for a half hour, provided a thick triple mat of asbestos is used and not too strong a suction is applied. Since the precipitate is colloidal in nature, it should not be washed with pure water. Wash waters containing silver are unsuitable because of the fact that the excess of silver in the precipitate must be washed out completely before titration, while those containing potassium salts tend to replace silver. For these reasons a wash solution consisting of ice water to which a few drops of acetic acid have been added has been selected. (Not more than one cubic centimeter of glacial acetic to one-half liter). The precipitate is washed until the wash water is colorless, and finally with about one hundred cubic centimeters more. Because of the danger of having the colloidal substance pass through the filter the latter should at no stage be permitted to drain completely.

The precipitate, together with the Gooch, is transferred to the casserole in which precipitation took place and oxidized with a hot standard solution of KMnO_4 (N/10), the latter being diluted to any convenient volume. Titration is carried on in acid solution, about ten cubic centimeters of 1:5 sulphuric acid being added. The solution is heated to boiling, oxidation being complete after a few minutes. The excess of KMnO_4 is titrated with an excess of standard oxalic acid and the solution titrated back to color with KMnO_4 .

Following this determination of NO_2 , the asbestos is filtered off upon a Gooch, washed, and reserved for repeated use. The silver in the filtrate is titrated with a standard NaOHS solution (approximately .02 N) using ferric alum as indicator. The latter titration should not take place in hot solution.

In the results recorded in this paper, corrections have been applied for the reducing power of the asbestos used as well as for the sulpho-cyanide end point. Such correction amounted to about one tenth of a cubic centimeter in each case.

Method of Calculation Since the relation of K + Ag to NO_2 titrated is a constant quantity, we can, after having determined both Ag and NO_2 , calculate the amount of potassium present, the ratio of metal to determined nitrite being taken as 1:1.9. Thus we can calculate the amount of nitrite equivalent to the silver titrated. Subtracting this value from the total nitrite titrated by KMnO_4 , we obtain the amount of the latter equivalent to potassium. Potassium is calculated from the remaining nitrite, using the ratio 1 K = 1.9 NO_2 . Factors may be used to simplify the calculations. It is suggested to anyone wishing to use this method extensively, that the nitrite factor (found to be 1.9 in our case) be redetermined. In this manner any error in preparing the standard solutions will be partly counterbalanced. Determination No. 14 (See Table 4) will be recalculated here as an example. The following data is known.

$$1 \text{ cc. N/10 KMnO}_4 = .0023 \text{ gm. NO}_2.$$

1 cc. .02534 N NaCNS = .002734 gm. Ag = .002215 gm. NO_2 .

1 gm. NO_2 = .4474 gm. K.

Example:

21.64 cc. N/10 KMnO_4 = (21.64 x .0023) = .04977 gm. NO_2 .

12.50 cc. (.02534 N) NaCNS = (12.50 x .002215 = .02769 " "

Difference = .02208 " "

.02208 x .4474 = .00988 gm. = wt. of K

It is interesting to note that we could prepare a NaCNS solution of such a strength (exactly .0263 normal) that one cubic centimeter N/10 KMnO_4 will be equivalent to one cubic centimeter of NaCNS. The calculation will thus be greatly simplified: thus--(Vol. N/10 KMnO_4 - Vol. NaCNS) (factor) = wt. K

Known solutions containing varying amounts of potassium up to .04 gram were analysed according to the procedure described above, the total volume at the time of precipitation being one hundred cubic centimeters in each case and the concentration of silver being approximately two onehundredths normal. The results given in Table 4, show that the agreement between the calculated and determined values is satisfactory, and also that the ratio stated above holds over a considerable range. The larger differences obtained when dealing with the greatest quantity of potassium (.04 gms.) may be due to increased difficulty in washing although a probable source of error is pointed out in the following paragraph.

TABLE IV

No.	Amt. K present	Cc. N/10 K ₂ CrO ₄	Cc. NaCNS .02534 + N	Amt. K found	Error
6	.0005 gm.	1.13	.65	.0005	.0000
7	.0005	1.20	.82	.0004	- .0001
8	.0010	2.37	1.53	.0009	- .0001
9	.0010	1.75	.97	.0008	- .0001 +
10	.0020	5.08	3.30	.0019	- .0000 +
11	.0020	5.02	3.15	.0020	+ .0001
12	.0060	13.32	7.95	.0058	- .0002
13	.0060	11.91	6.40	.0059	- .0001
14	.0100	21.64	12.50	.0099	- .0001 +
15	.0100	19.70	10.50	.0098	- .0001 +
16	.0140	28.91	15.90	.0140	- .0000
17	.0140	27.42	14.50	.0138	- .0002
18	.0200	41.29	22.40	.0203	+ .0003
19	.0200	39.69	21.00	.0200	.0000
20	.0400	72.20	38.10	.0396	- .0005
21	.0400	77.98	39.40	.0412	+ .0012

The amount of silver contained in the precipitate varies with the concentration of the silver in the solution in which precipitation takes place, a corresponding variation in the permanganate value being observed. This interesting fact may even be noticed in the results of Table 3, in which case the silver value had been constant. The concentration of silver may be varied from .01 normal to almost .03 normal without impairing the accuracy of results by this method. However, because of the ease of adjusting the silver concentration to any approximate value we would recommend the use of a .02 normal solution.

Our work with low concentrations of silver has shown that, when dealing with small amounts of potassium, (less than

.01 gm. per 100 cc.) no variation is noted. With greater concentrations of potassium, however, there is a slight tendency toward high results due to the carrying down of a trace of sodium. This can be prevented by using a larger concentration of silver, or by allowing the precipitate to stand for about an hour in the presence of a slight excess of silver, and thus replacing any trace of sodium carried down. This latter point should be borne in mind even when working with the proper concentrations; particularly so when potassium is high. Under any conditions, it will be found desirable to precipitate not more than .02 gm. K in one hundred centimeters of .02 normal silver nitrate. The high result obtained in determination No. 21 (Table 4) is thus readily explained, since the precipitate in this case was filtered immediately. Because of the large amount of potassium present, the concentration of silver at the end of the precipitation was less than .01 normal.

The effect of the presence of varying quantities of sodium on the accuracy of the method was next studied. The results in Table 5 show that even when the ratio of potassium to sodium is one to five hundred, no appreciable error is introduced.

That no interference need be feared when moderate quantities of the alkaline earth metals are present is shown by the results recorded in Table 6. The analyses were carried out in the presence of varying quantities of calcium and magnesium

salts. No determinations were made in the presence of barium or strontium salts, but it is quite certain that they would not interfere unless present in large quantities, when a barium or a barium silver cobaltinitrite may be precipitated.

TABLE V
(Showing Effect of Presence of Sodium)

No.	Amt. K present	Amt. Na present	Cc. KMnO_4 N/10	Cc. NaCNS .02534 N.	Amt. K found	Error
91	.0020 gm.	.200 gm.	4.69 cc.	2.83 cc.	.0020 gm.	.0000
92	.0020	1.000	4.26	2.45	.0019	-.00005
93	.0200	.200	39.71	20.60	.0202	+.0002
94	.0200	1.000	38.41	19.65	.0200	.0000

TABLE VI
(Showing Effect of Presence of Ca or Mg)

No.	Amt. K present	Amt. Ca or Mg present	Cc. KMnO_4 N/10	Cc. NaCNS .02534 N.	Amt. K found	Error
95	.0020	.100 gm. Mg.	3.85	1.90	.0021 gm.	+.0001
96	.0020	.100 Ca	4.05	2.15	.0020	+.0000
97	.0020	.500 Mg	3.85	2.00	.0020	.0000
98	.0020	.500 Ca	4.42	2.80	.0021	.0000
99	.0200	.500 Mg	38.62	19.60	.0203	+.0003
100	.0200	.500 Ca	40.93	21.70	.0206	+.0006

APPLICATION OF THE METHOD TO THE DETERMINATION
OF POTASSIUM IN MINERAL WATERS

With the co-operation of the State Water Survey, the cobaltinitrite method, as described above, was applied to the determination of potassium in mineral waters. Eight waters were analysed for complete mineral content by Mr. H. L. Olin, using the methods commonly employed in the laboratory of the Water Survey. Since it will be of interest to observe the widely varying conditions under which the method has been applied, the complete mineral analysis is given in Table VII.

The results obtained by the cobaltinitrite method will be compared with those obtained by careful analyses of the same waters by the chloroplatinate method. In order to make the test as rigid as possible, waters differing greatly in mineral content have been selected.

It has already been shown that the presence of moderate quantities of the alkaline earth metals and sodium, do not interfere with the qualitative detection of potassium. To see if the presence of these metals has any effect on the quantitative determination the waters were analysed for potassium, both in the presence of all the other dissolved materials and after a separation of the other metals by means of barium hydroxide and ammonium carbonate.

TABLE VII

Complete Mineral Analysis
(Expressed in milligrams per 1000 cc.)

No.	1	2	3	4	5	6	7	8
Residue at 100 °C.	942	1111	12,567	2090	2358	615	3663	5426
Potassium	14.8	15.7	119.3	19.4	2.0	1.3	23.4	14.2
Sodium	276.6	313.3	3844.3	445.1	354.3	26.4	967.4	2121.4
Ammonium (NH ₄)	1.0	1.0	3.6	1.0	2.5	.14	1.6	.9
Magnesium	14.4	28.8	131.5	56.2	102.4	30.5	74.1	14.5
Calcium	50.4	56.4	665.0	200.0	283.0	129.6	168.0	25.7
Iron and Aluminum	1.5	1.5	4.9	1.7	12.0	3.0	1.5	.6
Chlorine	325	400	6916	1000	750	140	340	2560
Sulphate	7.3	41.6	423.3	118.4	497.4	54.4	1363	.0
Silica	10.6	8.8	9.4	10.4	20.0	1.4	12.0	10.0

It is evident that waters have been selected showing a wide variation in their mineral constituents. The results on the determination of potassium were performed either in duplicate or triplicate by each method. In the chloroplatinate method the precipitate was washed free from sodium with eighty percent ethyl alcohol and then collected on a Gooch-Monroe crucible. Any insoluble impurity was corrected for by redissolving the precipitate in hot water and weighing the residue. The analyses by the cobaltinitrite method were made both with and without the separation of the other metals. The procedure is as follows: The combined chlorides of sodium and potassium are dissolved in about seventy five cubic centimeters of water, the chlorine precipitated by adding an excess of silver nitrate, and the silver chloride filtered off. One cubic centimeter of the filtrate (drawn off

with a pipette) may be titrated with the standard sulphocyanide solution in order to determine approximately its strength in respect to silver. Enough tenth normal silver nitrate is then added so as to obtain approximately a .02 normal silver solution in which to precipitate the potassium. The analysis is conducted as has been outlined above.

When it is desired to precipitate potassium from a mineral water without a previous separation of the other metals by the ammonium carbonate method, a convenient quantity of the water (usually 500 cc.) is evaporated to a small volume in a cassérole--the chlorine precipitated, and the determination completed in the usual manner.

It is necessary to allow the solution to cool to room temperature (20° to 25° C.) before precipitation, because of the increase in solubility of the precipitate at higher temperatures. The solution should be neutral or acid with acetic acid. Results of these analyses are shown in Table VIII.

TABLE VIII
Potassium in Mineral Waters

Lab. No.	Results by platino-chloride method			Results by cobalti-nitrite method. No separation of other metals			Results by cobalti-nitrite method. Separation of metals		
	Milligrams per 1000 cc.			Milligrams per 1000 cc.			Milligrams per 1000 cc.		
	Average			Average			Average		
1	13.0	14.6	14.8	14.7	14.9	14.8	14.8	15.2	15.3
2	13.4	13.4							
		15.3	15.7	13.2	13.5	13.4	16.2	16.7	16.5
3 [#]	117.0	121.	119.3	119.8	117.5	118.7	124.	122.	123.
4	19.4	19.4	19.4	20.3	20.0	20.2	21.7	21.9	21.8
5	1.8	2.2	2.0	1.4	1.3	1.4	1.8	1.5	1.7
6	1.1	1.4	1.3	.9	1.2	1.1		1.1	1.1
7	26.2	25.5	26.4	26.3	26.2	26.3	26.0	26.4	26.2
8 [#]	15.0	13.4	14.2	12.0	11.0	11.5	12.6	13.0	12.8
9	13.9	14.3	14.1	14.0	14.0	14.0	15.2	15.3	15.3
10 Univ. Supply			1.4			1.4			

[#] Only 100 cc. portions of the water were analysed.

These results show excellent agreement and demonstrate that the new volumetric method is capable of giving results of a high degree of accuracy. The values obtained after the separation of the heavy metals are in nearly every case slightly higher than those obtained without such a separation. A careful examination of the chemicals used showed that they did not contain potassium. The reason for this slight increase has not yet been explained. In waters No. 3 and 8, because of the very large mineral content, only one hundred cubic centimeters were taken for analysis by the chloroplatinate method, and consequently the results contained in the table are ten times those actually

determined and are correspondingly less exact. In the other cases five hundred cubic centimeters were analysed in each case. The results by the cobaltinitrite method were obtained from liter or half liter samples.

INVESTIGATION OF THE PLATINIC CHLORIDE METHOD

It was noticed that if the filtrates and washings from the chloroplatinate determinations were evaporated to dryness (using alcohol for the reduction of the platinic chloride) and the residue taken up with water, potassium could be detected in this solution. The following series of analyses was therefore made, the potassium being determined by the usual procedure for the chloroplatinate method, but the filtrate and washings were collected and analysed a second time by the cobaltinitrite method. The results are given in Table 9. They show that a fair degree of accuracy can be expected from the platinic chloride method even when in the presence of a great excess of sodium, although, to be sure, slightly low results are obtained, the potassium being completely recovered from the filtrate by means of the cobaltinitrite method. This is in agreement with the experience of the Bureau of Chemistry¹, which recommends that a correction of + .0008 gm. KCl (equivalent to .0004 gm. K) be applied to determinations by this method.

1. U.S. Dept. of Agr. Bull. No. 91, pp. 30 (1905).
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TABLE IX

No.	Amt. K present	Amt. Na present	Amt. K found as K_2PtCl_6	Error	Amt. K found in filtrate by cobaltinitrite method
1	.0400 gm.	None	.0396 gm.	- .0004 gm.	.0007 gm.
2	.0400	None	.0395	- .0004	.0005
3	.0200	None	.0200	.0000	.0002
4	.0400	.0400 gm.	.0397	- .0003	.0004
5	.0400	.200	.0394	- .0006	.0005
6	.0400	.200	.0394	- .0006	.0005

THE ANALYSIS OF SILVER POTASSIUM COBALTINITRITES

Several analyses of the silver potassium cobaltinitrites above described have been made and some of the results will be given here, although no definite conclusions can be drawn at present.[#] It is, however, clear that the compound does not have the simple formula ordinarily assigned to cobaltinitrites; i.e. $M_3Co(NO_2)_6$. The precipitate will be analysed again before drawing conclusions. The work of previous investigators in this field on the analyses of other cobaltinitrites will be repeated in order to determine whether or not the deviation from the accepted formula is characteristic of the silver potassium salt alone. A preliminary experiment leads us to believe that the tripotassium salt, $K_3Co(NO_2)_6$, may agree with the silver potassium

[#] The fact that a definite amount of silver, in the silver potassium salt, is displaced when washing with solutions containing potassium salts, may be of value in determining the structure of the compound itself.

salt, in as far as the ratio of cobalt to nitrite is concerned. The results of this work are given in the next section on the determination of cobalt.

Preparation of the Precipitate for Analysis

The silver potassium salt was precipitated as in the case of the quantitative determination described above; i.e. 10 cc. potassium nitrate solution (.020 gm. K) + 20 cc. tenth normal silver nitrate were diluted to a volume of one hundred cubic centimeters, and the potassium precipitated by adding the freshly prepared reagent (25% solution) drop by drop with stirring. About four cubic centimeters, of the latter were used. The precipitate was separated out by whirling in a centrifuge, two liters of solution being used at a time. It was then washed three times with one hundredths normal silver nitrate solution and finally twice with absolute alcohol, using the centrifuge each time. In order to hasten the drying, the precipitate was treated with ether several times and finally preserved in a vacuum desiccator.

Method of Analysis

A weighed portion of the precipitate was decomposed by warming with ten cubic centimeters of concentrated nitric acid, the solution diluted to at least fifty cubic centimeters and the silver precipitated by the addition of fifth normal hydrochloric acid. The silver chloride was filtered on a platinum Gooch-Munroe crucible and weighed. The filtrate and washings

from the silver chloride were collected, evaporated with sulphuric acid in order to decompose the nitrates, and the cobalt determined (in ammonia solution) by the usual electrolytic method. Nitrite was determined in a new portion of the sample by the permanganate method described on page 21. Total nitrite was determined by the aluminum reduction method in alkaline solution. The alkaline metals were determined in a third portion of the sample after the precipitation of the silver as silver chloride and the separation of the cobalt as sulphide. Both the platonic chloride and the volumetric cobaltinitrite methods were used.

In repeating the analyses a slightly modified procedure will be used, silver, cobalt and potassium all being determined in one sample. The cobalt will be weighed as sulphate after its separation as sulphide.

Results of Analyses

	1	2
Silver	25.87%	25.86%
Cobalt	10.65	10.81
Nitrite (titrated)	42.34	42.45
Nitrite (total)	46.45	46.40
Potassium (as $K_2P + Cl_6$)	10.27	9.80
Potassium (as cobaltinitrite)	10.04	10.10
Sodium plus impurities	.1	.1

Water may be found by difference.

These preliminary analyses, although not as accurate as might be desired, show definitely that in the silver potassium cobaltinitrites the ratio of metal to total nitrite is not 1:2

as given by the general formula $M_3Co(NO_2)_6$, but somewhat higher." Neither is the ratio of cobalt to total nitrite 1:6, but is found to be considerably lower (about 1:5.5). The analyses agree, although not as closely as is desired, with the corresponding ratios found when using the cobaltinitrites in quantitative work. (See page 19 and page 36). The difference between titrated and total nitrite shows definitely that cobalt is in the oxidized state.

THE QUANTITATIVE DETERMINATION OF COBALT

Although cobalt may be quantitatively separated from nickel as cobaltinitrite, no successful determinations of cobalt have been made in which the latter was determined directly. (The work of Erdmann¹, of Rose² and that of Gaube³ may be taken as fairly characteristic.)

In the following preliminary determinations, the potassium cobaltinitrite ($K_3Co(NO_2)_6$?) was titrated directly. The silver potassium salts will be used later. A solution of cobalt nitrate (standardized by determining the cobalt as cobalt sulphate) was used. A known amount of the latter in about fifty cubic centimeters of thirty percent potassium nitrite solution, was

The above formula requires the ratio of metal to titrated nitrite to be 1:1.83. The true ratio is very close to 1:1.90, and that found according to the above analysis is 1:1.87.

1. J. prakt. Chem., 97, 385.
2. Pogg. Ann., 110 411.
3. Z. anal. Chem., 5, 74-75.

acidified by the addition of enough glacial acetic acid to liberate the nitrite. When the yellow potassium salt had completely precipitated, it was filtered on a Gooch, washed with dilute potassium nitrate solution and titrated in the usual manner.

Results:

No.	Wt. Co used	Cc. N/10 KMnO_4
1	.0200 gm.	34.28
2	.0200	34.42
3	.0200	34.50
4	.0200	34.45

The constant results obtained suggest the possibility of a quantitative determination of cobalt based on the above method. More interesting still is the fact that the ratio of cobalt to total nitrite is found to be about 1:5.6 and not 1:6 as demanded by the formula of the tripotassium salt. This work will be repeated in connection with the analysis of the various cobaltinitrites, and hence no final conclusions will be drawn at present.

SUMMARY

- (1). A review of the previous work on cobaltinitrites (as given in the writer's first thesis) has been given.
- (2). The new silver potassium cobaltinitrites have been described.
- (3). They are recommended as a delicate qualitative test for potassium. Directions for applying the test, its delicacy, and all interferences have been given in detail.

- (4). The corresponding silver salts with ammonium, rubidium, cesium, thallium, and lead are mentioned, and the possible use of some of them in analytical work, indicated.
- (5). A corresponding series of double salts with lead and the alkali metals has been prepared.
- (6). A new volumetric method for the quantitative determination of potassium, based on the insoluble silver potassium cobaltinitrites, has been described.
- (7). It was shown that sodium, calcium and magnesium salts do not interfere with the quantitative method unless present in very large amounts.
- (8). The method has been applied to the analysis of mineral waters and results obtained which compare favorably with those obtained by the standard method.
- (9). It was definitely shown that the slightly low results obtained with the chloroplatinate method are due to the solubility of the potassium chloroplatinate, since the potassium may be determined in the filtrate by means of the cobaltinitrite method.
- (10). A preliminary report has been made in regard to a quantitative volumetric determination of cobalt.

ADDITIONAL REFERENCES

The following references, dealing mostly with the analyses of cobaltinitrites, a detailed review of which has been given in the first thesis already referred to, are mentioned here for the convenience of the reader.

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